JAPANESE [JP,07-150419,A]

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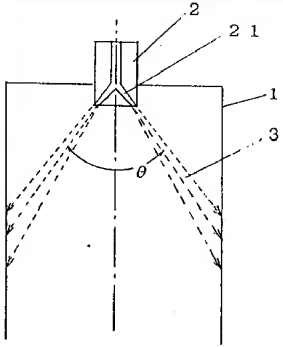
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to carbon fiber and the method of manufacturing carbon fiber with the vapor phase growth by the pyrolysis of an organic compound in more detail. [0002]
[Description of the Prior Art]Although it is the outstanding method of the method of manufacturing carbon fiber with vapor phase growth carrying out the pyrolysis of the organic compound in a heating furnace, and obtaining carbon fiber at one process, there is a problem in industrial productivity and improvement improvement has been made. For example, after making the ultrafine particle of the transition metal adhere to a ceramic substrate in the beginning, it was

Drawing selection
Representative drawi



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the method of supplying an organic compound, making it decomposing, making it growing up for a long time, and manufacturing comparatively thick long gaseous phase method carbon fiber. Although the carbon fiber of good physical properties was obtained, when this method became thick, its reaction velocity was low and was insufficient for industrial production. In order to improve this productivity, in JP,58-180615,A, the gas flow method in which the superfines end of a transition metal or its compound is made to exist so that it may float in the thermal decomposition zone region of an organic compound is proposed. As a gas flow method, these metal particles are adjusted to JP,63-92726,A so that it may be set to 2-30 nm, this is distributed in the liquid of an organic compound, and although a drop is used and being supplied in a furnace, it is said that it is preferred to adjust the path of a drop in that case. Similarly it is said to JP,62-53419,A that it is good for the path of a drop to be 30 micrometers or less. In these cases, the drop is supplied so that it may spread in the whole reaction zone, as usually shown in drawing 2. The method of making the organic compound of transition metals, such as ferrocene, into the gaseous phase at JP,4-24320,B, leading to the deposit zone of carbon fiber, depositing on a substrate the ultrafine particle of the metal which carried out the pyrolysis and was generated there, and growing up carbon fiber there is indicated.

[0003]

[Problem(s) to be Solved by the Invention]Since the length direction of a furnace and parallel are supplied, carbon fiber is generated by a floating state, many are taken out out of a furnace as it is, and reaction time is short, the organic compound (raw material) which contains a transition metal or its compound in a gas flow method has a low reaction yield, Carbon fiber with them was not obtained. [the small thickness or length of carbon fiber, and] [good / crystal growth is insufficient, and] Since it is not spraying so that ferrocene etc. may be concentrated on a substrate by the method of JP,4-24320,B. The concentration on the substrate of metal particles and a capacity factor are low, and since a raw material is gasified and is led in a furnace, again. Gas concentration becomes uniform in a furnace, concentration of the particles especially on a substrate and raw material concentration of the particle circumference cannot be made

high, and the yield of the carbon fiber on a substrate does not go up as these results.

[0004]When supplying a raw material to a reaction region by a drop, the energy which a reaction takes will be absorbed with radiant heat or the flow heat transfer of carrier gas. In order for temperature to rise to a reaction region in that case in a drop, when the quantity of heat and evaporation heat which are first required by the evaporating temperature of a fluid are required and heat supply is insufficient, a temperature fall is caused selectively, as a result, carbonization speed is lowered, conversion and a textiles growth rate fall, and the textiles of sufficient length are not obtained. Therefore, in order to gather the transmission speed of lengthening holding time of textiles in order to solve these problems, and reaction temperature, it is desirable to adopt the method of using together flow heat transfer and not only a radiant heat transfer but the thermal conduction from a furnace wall. An object of this invention is to provide the carbon fiber which aimed at growth of carbon fiber, and increase of yield by high concentration-ization of the raw material in the predetermined heat transfer and carbon fiber generation zone from holding time and a furnace wall, and was excellent in the characteristics, such as heat conduction.

[0005]

[Means for Solving the Problem]Raw material concentration near the furnace wall is made high by adopting a method of making a furnace wall generate carbon fiber and holding so that heat transfer may be improved instead of a substrate in this invention and predetermined holding time can be taken in order to solve an aforementioned problem, and carrying out by making supply of a raw material into a drop and spraying towards a furnace wall. Namely, in a method of this invention considering an ultrafine particle of a transition metal as seed, and manufacturing carbon fiber by a pyrolysis of an organic compound, Turning a minute drop of an organic compound containing a transition metal or its compound to a heating furnace wall surface, and spraying it continuously or intermittently. It is a manufacturing method of gaseous phase method carbon fiber making it react, making a furnace wall surface generate carbon fiber, making branched state carbon fiber generate on the carbon fiber further, and scratching this intermittently. It is desirable to

be able to heat-treat carbon fiber obtained here above 1000 **, and to grind it after heat treatment further.
[0006]This invention is explained in detail below. a transition metal which is seed and serves as a catalyst, or its compound -- the [periodic table] -- elements of IVa, Va, VIa, VIIa, and a group VIII, those alloys and mixtures, inorganic matter of those, and an organic compound are suitable. To a transition metal which serves as ultrafine particle seed (seed) of a transition metal element especially, and its compound, organic compounds, such as superfines (30 nm or less), such as Fe, nickel, and Co, ferrocene, and NIKKERUSEN, are preferred. Although superfines, such as Fe, nickel, and Co, have problems, such as a process top and condensation, especially since ultrafine particles, such as Fe, generate organic compounds, such as ferrocene, by a pyrolysis, they are preferred. As content of a transition metal as a catalyst, it is 0.1-5.0 preferably 0.03 to 10.0% of the weight to a carbon content (total quantity in which the carbon was included in use of ferrocene etc.) of an organic compound. Weight % is good.
[0007]In an organic compound used as a raw material of carbon fiber, it is [benzene, toluene, xylene, methanol, ethanol naphthalene, phenanthrene, cyclopropane, cyclopentene cyclohexane, other organic compounds and those mixtures, / volatile oil, kerosene] usable. Especially aromatic compounds, such as benzene, toluene, and xylene, are especially preferred. It distributes or dissolves, and it is liquid drop-like and compounds, such as an ultrafine particle of said transition metal or ferrocene, are supplied to this organic compound. an organic compound -- the whole quantity -- although it may be made such a drop, it is also possible to supply independently by that the remainder is liquefied or a gas, using one copy as a drop.
[0008]In order to raise crystal growth speed, it is necessary to raise concentration of an organic compound near the catalyst (seed) surface. Evaporating raw material liquid, in the case of a method of supplying with a gas, raw material concentration in a reactor including the surface of a catalyst turns into average concentration. However, since particles will arise from there and liquid will evaporate simultaneously if it supplies by a drop, raw material organic compound concentration near the catalyst becomes quite high, and results in raising the rate of crystal growth. It was

one of the features of this invention, and in this invention, a feeding method of a drop is also turned to a furnace wall, and supplied a drop continuously or intermittently. Since a furnace is usually an outside heat method, heat in a furnace is supplied by heat transfer of radiation or gas from a furnace wall. Therefore, it is more advantageous to heating for a drop to be a furnace wall and near it. After carbon fiber's generating to a furnace wall and covering a furnace wall, a drop is sprayed on these textiles, but since thermal conductivity is dramatically large, this carbon fiber does not become disadvantageous for heating of a drop.

[0009]When thermal conductivity becomes good, after growth of textiles speeds up and textiles generate to a furnace wall, spray a drop on it and generation of textiles including branching and also spraying of a drop are performed continuously, but. Since particles arise between accumulated textiles or on textiles, a capacity factor of particles increases and it is thought that it is a cause of an increase in yield. A method of spraying an organic compound in which a method of supplying a drop contains a transition metal or its compound using a spray nozzle is suitable. Although spraying may spray this drop as it is, since hydrogen gas is usually used as carrier gas, it is preferred to spray this hydrogen gas using a spray nozzle which can be sprayed together. It is considered as a structure inclined so that a passage of a fluid at a tip of a nozzle might be extended radiately to make it spray spraying on a furnace wall.

[0010]A schematic diagram of a device used for operation of this invention is shown in drawing 1. 1 is a heating furnace in a figure, and this has a preferred vertical mold like a graphic display by an ease of dropping [scratch] textiles and the circumference of a furnace wall which were deposited on a furnace wall becoming the same conditions etc., although a horizontal type is not impossible, either. 2 has structure where the lower part 21 of a fluid channel inclines by a pressure type distribution spraying nozzle, and a fluid spreads radiately. This passage lower part 21 is the structure where some stomata are provided. A fluid which dissolved ferrocene etc. is supplied to a nozzle with carrier gas, and is sprayed by a pressure of carrier gas. As for the vertical angle, 30-120 degrees is preferred by a fluid in which 3 was sprayed by a diagram.

[0011]Carrier gas is used when gas of reduction nature including hydrogen (H_2) gas supplies a raw material and a catalyst to a thermal decomposition zone region preferably for an activity manifestation as a catalyst of a transition metal, and maintenance. A 1-70-mol part is suitable for quantity of carrier gas to the organic compound 1. 0-mol part which is a carbon source. A size of a drop introduced into a reaction region influences thickness of textiles, length, and conversion with regards to a size of a core of a catalyst. If a size of a core of a catalyst is large, thickness of textiles will become thick, and if length is conversely small short, it will become thin weak textiles. Since a lot of evaporation energies are needed when particle diameter of a drop is large, a partial temperature fall is caused and it leads to decline in conversion, or a fall of a deposition rate of carbon fiber. A rate evaporated before evaporating immediately after introduction and reaching a wall surface, if too small becomes high. 70-200 microns is suitable for a path of a minute drop sprayed when the above points were taken into consideration.

[0012]Spraying of a drop is performed continuously or intermittently. Therefore, since carbon fiber generates to a furnace wall surface at first and it is further sprayed on the textiles, many of textiles generated there serve as branched state. Thus, generation growth of textiles takes place in a furnace wall surface, and it deposits on a wall of a furnace. It is failed intermittently to scratch this. Although an interval which it fails to scratch looks at and determines a deposition situation, a range for about 15 minutes is suitable for it from 10 seconds. The method of failing to scratch can use a jig which attached a ring at a tip of a stick (publication of unexamined utility model application Showa 62-93379). Temperature of a wall of a furnace is about 800-1300 ** as well as the usual case. Most carbon fiber obtained by this invention is thickness of 0.05 to 0.5 microns, and the length 1-100micro.

[0013]

[Function]space productivity is improved -- it should make -- a raw material -- a furnace -- internal division -- in supplying the whole solution zone, it is easy to produce temperature distribution in this thermal decomposition zone region at the radial direction and also longitudinal direction of a furnace, and it becomes an uneven cause. Although it is

desirable to carry out to the most uniform possible temperature zone as for supply of a raw material, even if it controls heat tracing by the endothermic or exoergic reaction under reaction, it is difficult to maintain a more uniform temperature zone widely. Carbon fiber is made to generate in this invention in a furnace wall surface. Therefore, a heat transfer system can introduce not only radiation but the conduction system from a furnace wall. The thermal conductivity of carbon fiber is remarkably large, by introducing conduction, compared with the case where carbon fiber is made to generate within [whole] a furnace like a gas flow method, the heat transfer of heat becomes good, homogeneity becomes good, and, in addition to radiation, reactivity and the growth possibility of textiles become good.

[0014]By supplying a raw material by a drop, the concentration of the metaled carbon compounds of the particle circumference increases, and yield also improves. A raw material including a catalyst is sprayed on the surface of carbon fiber grown-up on a substrate or a substrate, growth of the textiles is promoted in the process in which the evaporation reaction is carried out, and a crystal nucleus is newly made in a carbon fiber surface, and new growth is promoted with it as the starting point. Branched state gaseous phase method carbon fiber is obtained by this repetition.

[0015]

[Example]With reference to an accompanying drawing, the example and comparative example of this invention explain this invention in detail below.

As shown in example drawing 1, the spray nozzle 2 is attached to the crowning of the vertical mold heating furnace (17.0 cm in inside diameter, and 150 cm in length) 1. Temperature up and maintenance of the temperature of the inner wall of the kiln of the heating furnace 1 are done at 1200 **, and they are the spray nozzles 2-4. It supplies so that spraying (spray) spraying of the part for liquid material 20g /of the benzene containing the ferrocene of weight % may be directly carried out by the flow of hydrogen gas for 100L/at a furnace wall. The shape of the spray 2 at this time is cone flank shape (the shape of a trumpet thru/or the shape of an umbrella), and the vertical angle theta of a nozzle is 60 degrees. Under such conditions, the pyrolysis of the

ferrocene is carried out, it makes iron particles, and this was seeded (seed) and carried out generation growth of the carbon fiber from carbon by the pyrolysis of benzene. It manufactured continuously over 1 hour, failing to scratch the gaseous phase method carbon fiber grown-up by this method at intervals of 5 minutes. The microphotograph (x5000) of this carbon fiber is shown in drawing 3. About 30 g was heat-treated at 2400 ** among the obtained carbon fiber, this was mixed with PP resin (Showa Denko [K.K.] make: SMA410), and the fiber reinforced plastics containing 50wt% carbon fiber were manufactured. It was 0.14-ohmcm when volume ratio resistance of these fiber reinforced plastics was measured.

[0016]It presupposed that it is the same as the case of the example which mentioned the other manufacturing conditions above using the thing of a type as shown in drawing 2 which carries out the spray of the spray nozzle which carries out comparative example use all over directly under [of a furnace], and gaseous phase method carbon fiber was manufactured. The microphotograph (x5000) of the carbon fiber is shown in drawing 4. It was 0.40-ohmcm, when about 20 g of obtained carbon fiber was heat-treated at 2400 **, the fiber reinforced plastics which mix this with above-mentioned PP resin, and contain 50wt% of carbon fiber were manufactured similarly and volume ratio resistance was measured. The carbon fiber (drawing 3) obtained with the manufacturing method in connection with this invention has more branching than the carbon fiber (drawing 4) of a comparative example so that the microphotograph of carbon fiber may show. And although it is carbon fiber reinforced plastics, the carbon fiber of conductivity of this invention is better (specific resistance is small).

[0017]

[Effect of the Invention]As explained above, in the shape, homogeneity becomes good conventionally, the carbon fiber obtained by the manufacturing method concerning this invention has much branching, and since there is much a textiles comrade's relation, its conductivity improves and its dispersibility (mixing) with resin also improves. The effective carbon fiber as a micro raw material which functions as an addition-of-conductivity raw material in a composite material especially can be provided.

[Translation done.]